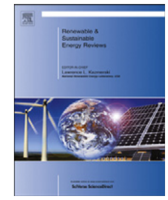
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A review on the role of materials science in solar cells

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The demand for energy of modern society is constantly increasing. The desire for environmental-friendly alternative energy resources with the least dependency on fossil fuels is growing. Solar energy is an important technology for many reasons and is worthy of urgent attention. Indeed, it has experienced rapid growth over the last few years. It is expected to become truly main stream when the breakeven of high performance is achieved and its cost becomes comparable with other energy sources. Various approaches have been proposed to enhance the efficiency of solar cells. This paper reviews some current initiatives and critical issues on the efficiency improvement of solar cells from the material sciences and chemistry perspectives.

Contents

1. Introduction . . . 5834
2. Identification of improved structures and base materials for solar cells . . . 5835
   2.1. Si . . . 5837
   2.2. GaAs . . . 5837
   2.3. CdTe . . . 5837
   2.4. Copper indium diselenide (CIS) and related compounds . . . 5838
   2.5. Organic and other solar cells . . . 5839
      2.5.1. Tandem cells and concentrating systems . . . 5839
      2.5.2. DSSCs . . . 5839
   2.6. Organic, Hybrid, and composite materials for solar cells . . . 5840
3. Advanced high-efficiency solar cell concepts . . . 5841
   3.1. Auger generation material . . . 5841
   3.2. Intermediate metallic band material . . . 5841
   3.3. Bandgap engineering . . . 5841
4. Cost and economic . . . 5843
   4.1. Materials consideration . . . 5844
5. Conclusion . . . 5845
References . . . 5845

1. Introduction

Energy experts predict that the world would need 30 TW of energy resources by the year 2050 to maintain economic growth (Fig. 1) [1]. A significant fraction of these new energy resources must come from renewable energies given their abundance and environment friendliness. Many scientists believe that the sun is the only candidate that can offer a fully developed solution for the energy crisis. Therefore, solar cells can be considered as a mainstream renewable energy resource once their manufacturing cost is decreased to an affordable level comparable with other available energy resources. Parida et al. [2] reviewed different issues

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concerning photovoltaic (PV) technologies. At this stage, new initiatives on harvesting incident photons with greater efficiency are needed to meet the global clean energy demand. First-generation (1 G) solar cell devices suffer from high manufacturing and installation costs, whereas second-generation (2 G) ones consist of less expensive polycrystalline semiconductor thin films. However, the efficiencies of the latter need to be enhanced for practicality. Currently, the focus is on third-generation (3 G) devices that can deliver economic, highly efficient cells that can emerge as a new technology in the near future (Fig. 2) [3]. Efforts are presently being exerted to address the following issues: (i) enhancing the efficiencies of cells compared with other competitors, (ii) making the cells cost effective for both secondary and primary power generation, and (iii) achieving objectives (i) and (ii) in manufacturing a single solar cell device/module and related processes [4,5].

The physics of solar cells is based on the PV influence, i.e., the generation, trapping, recombination, and transport of electron–hole pairs throughout the semiconducting material and within the contact electrodes. The chemistry of solar cells is affected by the material and its special in-homogeneities, such as defect chemistry, i.e., deviation from stoichiometry and doping mostly when dealing with unbalanced conditions [6]. High-level chemical purity is required for materials because even very minor impurities can significantly affect the material properties. The crystalline structure is also very crucial in crystalline semiconductors because defects in (such as dislocations, twins, and stacking faults) affect the semiconducting properties of a material [7]. The application of chemistry and physics in solar energy conversion is a great challenge. Nanotechnology [8] can also enable remarkable improvements in the efficiency and cost of solar power utilization [9]. At the microscopic level, the epi-structure of solar cells is an elaborate network of electron paths. Essentially, the sole function of a solar cell is the conversion of sunlight into electricity [10].

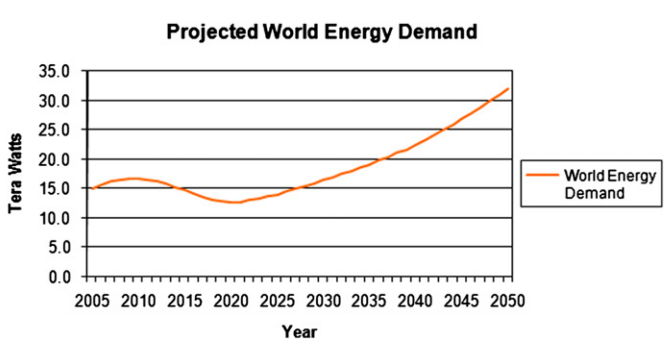


Fig. 1. Projected world energy demand.

Presently, the PV market relies on various technologies, including wafer-based crystalline silicon (Si) and Si thin films. The scope of these technologies and their possible futuristic options are grouped into current 1 G to future 3 G technologies [4,11]. In a thin film PV cell, a thin semiconductor layer of PV materials that can be from a few micrometers to even less than a micrometer is deposited on a low-cost supporting layer such as glass, metal, or plastic foil because thin-film materials have higher light absorptivity than crystalline materials. Thinner layers of semiconductor yield material cost savings.

Deposition techniques are cheaper and faster, making the mass production of thin film materials much easier than that of the crystalline Si. The main drawback in thin film PV cells is the non-single crystal structure of its materials, which results in low-efficiency cells. To overcome this problem, large areas that increase area-related costs such as mountings are required.

For the next decade, the entire focus of PV technology is on developing an efficient mechanism that can absorb all incident solar spectra and convert them to electricity through an integration technique for a series of photo-acceptors with different band gaps or absorption spectra.

Enhancing the regular crystalline structure using nanocrystalline materials can increase the absorbance of all incident solar spectra in thin films or multilayered solar cells. This increase requires an electrolyte to transfer the charge from the photo-acceptor to the electrodes in dye-based and polymer solar cells, whereas in nanoparticle-based cells, the particles should be sufficiently close to one another to transfer the charge directly. To achieve a reliable and cost-effective solar cell, the right combination of photo-acceptor, charge transfer structures, and electrodes within the structure of solar cells must be achieved.

However, efforts should be exerted to ensure that the development of these integrated structures is not too complex and can easily be upgraded to industrial-scale manufacturing without any compromise on the cost. Thus, this review aims to explore the role of materials science in advancing PV technology by reconsidering its constraints.

2. Identification of improved structures and base materials for solar cells

The quality of base materials plays a critical role in the performance of solar cells. The long carrier diffusion lengths and

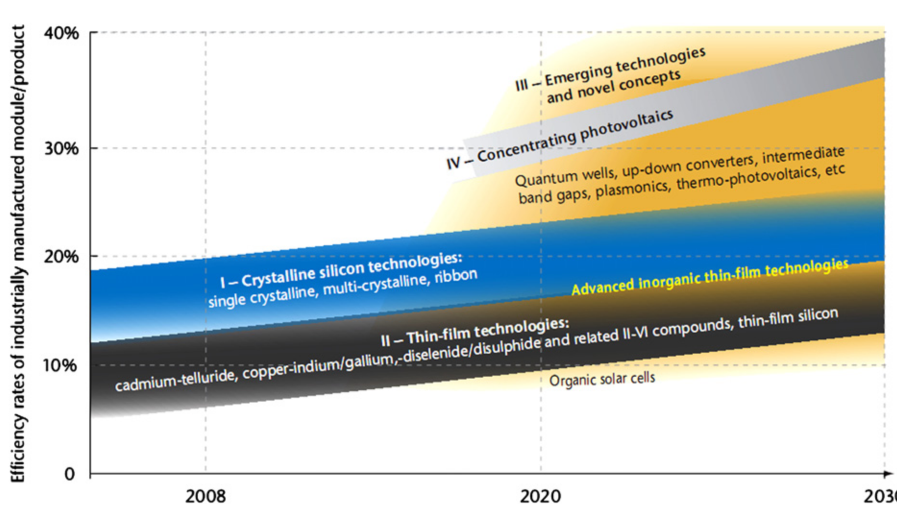


Fig. 2. Photovoltaic technology status and prospects.

bulk material, which are used as active layers in solar cells, must be defect-free. The surfaces and grain boundaries must be passivated consequently.

Table 1 summarizes some of the major requirements for the development of an efficient solar cell material system with some form of heterojunction [12]. Hence, many current and future investigations for finding new materials are expected.

Two common materials used in PV semiconductors are crystalline and thin films. Their efficiency and performance are calculated based on their light absorption and energy conversion efficiencies, as well as their manufacturing technology and production costs [9,13].

Ongoing research on PV can be categorized into three main areas, namely, development of cost-effective technology and/or improved efficiency to compete effectively with other energy sources, innovative technologies based on new solar cell architectural designs, and exploration of advanced materials that can serve as better light absorbers and charge carriers. Recently, significant progress has been made in improving the overall efficiencies of solar cell structures, including the incorporation of quantum dots (QDs), novel dyes, and multilayers of ultrathin nanocrystalline materials. A reported timeline of solar cell conversion efficiencies from 1975 to 2010 is shown in Fig. 3 [14].

Undoubtedly, there are abundant resources of such materials, which can be used to convert light into electrical energy. However, there is a serious deficiency in devices that can enable the cost-effective transformation of solar radiation into electrical energy with ~20% efficiency. One of the critical mechanisms of the PV effect is the generation of an internal electric field using a variety of dopants in different regions, contacts, surfaces, etc. to split electrons and holes. Consequently, the electrons and holes can contribute to the external circuit before their unwanted radiative recombination [15]. Some important methods that can allow the controlled design of semiconductor band gaps include the following: reduced dimensionality (nanomaterials), spontaneous ordering of semiconductor alloys to obtain new materials, as well as direct chemical synthesis of new interstitial compounds, new substitutional compounds, ordered vacancy compounds, and compounds based on *d* and *f* electron elements [16,17].

In 1993, Zunger et al. reviewed some of the important materials and structures for PVs [16]. The materials include non-traditional alloys, materials with reduced dimensionality, spontaneously ordered alloys, interstitial semiconductors, filled tetrahedral structures, ordered vacancy compounds, and compounds based on *d* and *f* electron elements. These new materials

Table 1
Criteria for choice of a heterojunction system for photovoltaic solar cells.

Property	Criteria
Band gap of smaller bad-gap materials	Band gap near 1.4 eV to maximize absorption of solar radiation, while minimizing diode current that limits V_{oc} Direct optical absorption so that carriers are generated close to the junction Long minority-carrier diffusion length
Band gap of larger band-gap materials	As large as possible while maintaining low series resistance
Conductivity type	Smaller band gap materials should usually be p-type because of longer electron diffusion lengths
Electron affinities	Materials should be chosen such that no potential spike occurs at the junction for the minority photoexcited carriers
Diffusion voltage	As large as possible, since the maximum Voc is proportional to the diffusion voltage
Lattice mismatch	As little mismatch in lattice constant between the two materials as possible (this appears to minimize interface state density and recombination losses through such states)
Deposition methods	Suitable deposition methods for thin-film formation and control should be available
Electrical contacts	It should be possible to form low-resistance electrical contacts to both n- and p-type materials
Materials availability	Supplies of the materials should be sufficient to allow large-area cell production
Material cost	Cost of the material should be competitive with alternative systems
Material toxicity	Material should be nontoxic, or control of toxicity should be possible
Cell stability and lifetime	Cell must have an operating lifetime sufficient to pay back economic and energy costs required to produce it

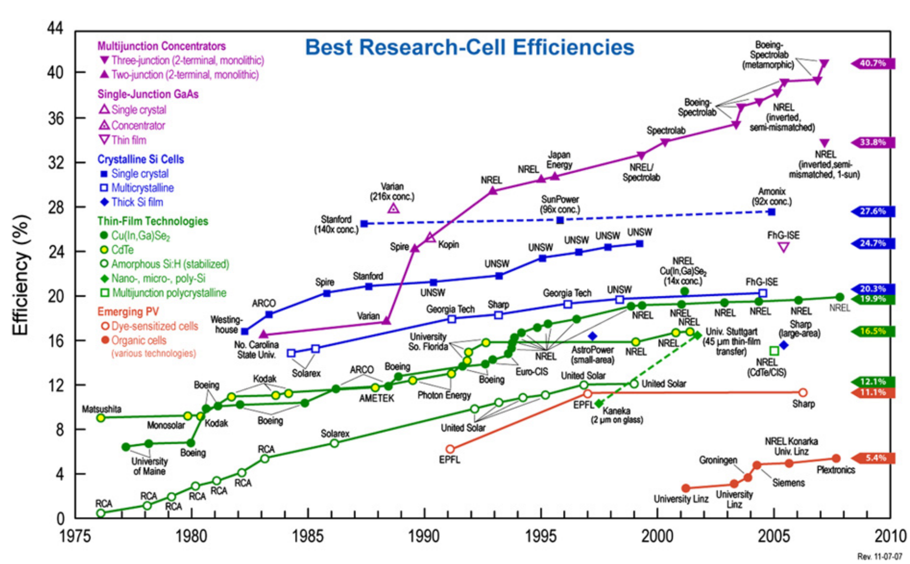


Fig. 3. Timeline of solar cell energy conversion efficiencies.

were designed to achieve simultaneous band gap tuning and lattice matching [15]. The relative probabilities of success are definitely related to the successful resolution of the various materials and crystal growth issues [18]. Some materials that have the potential to compensate for the aforementioned drawbacks include MoS_2 [19], WS_2 [20], and FeS_2 [21], as well as transition metal sulfides because they show favorable energy gaps for visible light conversion. Given that these are transition metal compounds, both surface chemistry and dopant chemistry are determined by coordination chemistry, which renders the required scientific approach different from that for classical materials such as Si, gallium arsenide (GaAs), and cadmium telluride (CdTe). For any photosensitive material to be developed in the future, quality control capable of achieving homogeneous photoactivity is expected to be a key factor. When preparing a photoactive material, a homogeneously distributed photosensivity cannot be assumed; thus, this factor must be optimized.

Nonetheless, numerous factors should be considered for these candidates to be viable for large-scale low-cost production. These factors include the (1) availability of raw material with sufficient quantities, (2) low-cost purification and deposition methods, (3) easy process control to obtain a large area product within the range of acceptable performance, and (4) large life expectancy of the finished solar cell [6].

Some materials are classified as thin films, such as inorganic layers, organic dyes, and organic polymers that are deposited on supporting substrates. The third group that uses QDs embedded in a supporting matrix by a "bottom-up" approach is configured as nanocrystals. Si is the only material that is well researched in both bulk and thin-film forms. There are many new alternatives to Si photocells, such as copper indium gallium selenide (CIGS), CdTe, dye-sensitized solar cells (DSSCs), and organic solar cells [22,23]. Most of them are directed at printing onto low-cost flexible polymer films, and ultimately, on common packaging materials. Among these new materials, semiconducting polymers are gaining much attention because of their large parameter space and inherent simplicity of device fabrication, and thus warrant further investigations [24].

To develop more complex materials, more studies on optical metamaterials, plasmonic materials, QDs, and bandgap-engineering materials should also be conducted [4]. Chemists are currently more interested in using templates the same as colloidal assemblies for the synthesis of advanced materials with enhanced or novel properties [25,26]. Recent advancements in templating methods for colloidal assemblies have provided the means for generating certain shapes independent of material composition and structure. Progress in the synthesis of "colloidal molecules" also provides new anisotropic building blocks suitable for the progressive construction of more complex colloidal oligomers, macromolecules, and crystals [27]. A collaborative effort among material predictors, material growers, and material characterizers holds promise for the successful identification of new and exciting systems [16].

Given that solar cells are intended for use under prolonged exposure to sunlight, another major challenge is their degradation with time. For instance, thin film materials especially chalcogenides, which are used in solar cells, must be protected carefully against oxidation. Instability problems play a dominant role in determining cell efficiency and utility. Bube [15] introduced a few other problems related to the likelihood of lattice mismatch at the junction between two semiconductors. This situation may by itself produce localized interface states that facilitate carrier loss through the recombination at a kind of "internal surface." Such localized interface states may also function in increasing the reverse saturation current density J_0, thereby reducing the open-current voltage $Ø_{oc}$. However, the proper deposition methods must be selected, the stability of materials must be improved, and defects must be minimized while considering materials chemistry. Quitoriano et al. [28] exploited the growth of high-quality semiconductors (Ge and Si) on amorphous and lattice-mismatched substrates using a metal-catalyzed, lateral semiconductor growth technique. They engineered the location of crystal nucleation by controlling the catalyst location, which can consequently avoid the formation of grain boundaries typical when crystals grow together. Considering that this technique can produce high-quality materials on inexpensive amorphous substrates, low-cost and efficient triple-junction PVs that can be used to build next-generation PVs can be realized. Fig. 4 summarizes the basic studies needed to develop solar cells with the most significant application in the next decade [29]. Some of the most important and fundamental PV materials and their related issues are listed below.

2.1. Si

Over 95% of all solar cells produced worldwide are composed of Si. The classical efficiency limit is currently estimated to be 29% [30]. Fig. 5 shows the photon flux as a function of wavelength [31]. Table 2 lists the data on different types of Si solar cells.

2.2. GaAs

The crystal structure of GaAs as a semiconductor compound is similar to that of Si. However, crystalline Si needs a thickness of 100 μm or more to absorb sunlight, whereas GaAs with a nearly ideal band gap of 1.43 eV only needs to be a few micrometers thick. With 25–30% energy conversion efficiency, GaAs exhibits a higher efficiency than crystalline Si. Since it is very resistant to heat and radiation damage, it is an ideal choice for concentrator systems and outer space applications. The expensiveness of single-crystal GaAs substrate is the main issue for the development of GaAs cells for terrestrial use. Two approaches to cost reduction include the fabrication of GaAs cells on low-cost substrates such as Si or germanium (Ge), and the growth of GaAs cells on removable GaAs substrate. This removable GaAs substrate can be reused to produce other cells, and even make GaAs thin films similar to CIGS and CdTe thin films [32].

2.3. CdTe

CdTe as a polycrystalline semiconductor has a high light absorptivity level, i.e., only about 1 μm thick can absorb 90% of the solar spectrum. Another advantage is its relatively easy and inexpensive manufacturing process. However, its conversion efficiency is low, similar to that of a-Si [13].

Some of the dominant problems of CdTe solar cell development include the difficulty of doping *p*-type CdTe, the difficulty in obtaining low-resistance contacts to *p*-type CdTe, the recombination losses associated with the junction interface [33], and cadmium toxicity-related precautions that have to be considered during the manufacturing process. The main problem in developing CdTe for PV application is the instability of cell and module performance. The fundamental mechanisms that govern carrier transport and the effects of the diffusion length L, depletion width W, and primary heterojunction vs. back junction on the CdTe thickness t or back contact have not yet been well investigated and understood [34].

Recently, Tang et al. [35] fabricated cadmium sulfide core/copper sulfide shell nanowire solar cells using a low-temperature solution-based cation exchange reaction. The open-circuit voltage and fill factor, which determine the maximum energy that a solar cell can produce, promote the inexpensive and convenient manufacturing method of nanowire solar cells. These new nanowire

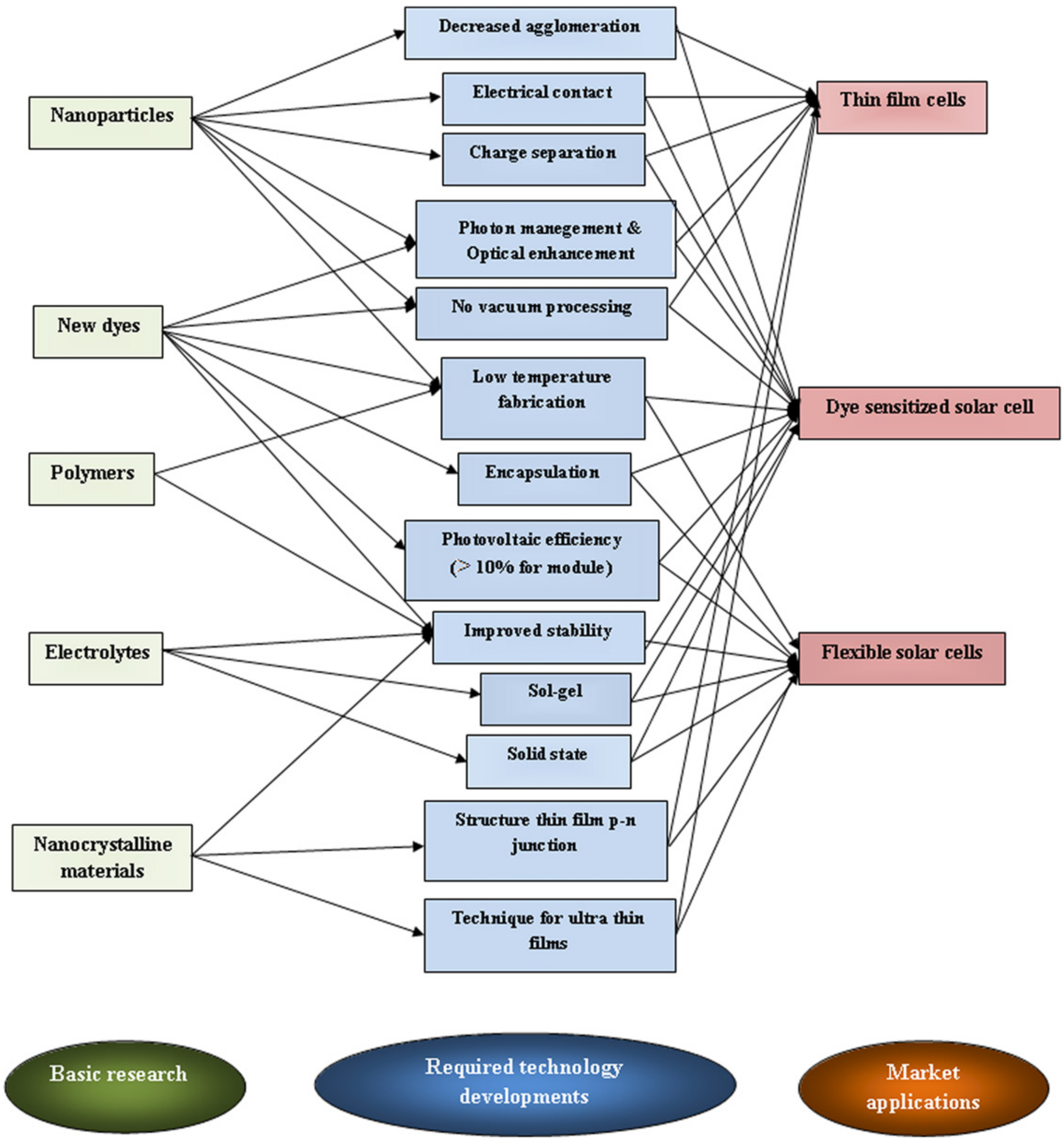


Fig. 4. Basic research underway with the technology developments required to achieve the desired applications.

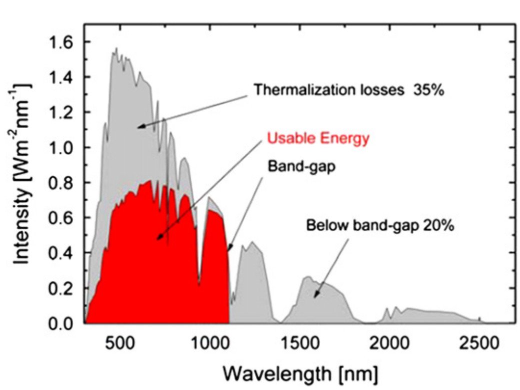


Fig. 5. Illustration of the principal losses incurred by a silicon solar cell. Photons with energies below the band-gap are transmitted straight through the device. Around 20% of the incident energy is lost this way. The energy of photons exceeding the band-gap is converted into heat. These thermalization losses account for around 35% of the incident energy. To achieve high efficiencies, novel concepts are needed to reduce these losses.

solar cells also demonstrate 5.4% energy conversion efficiency, which is comparable to those of planar solar cells.

The ability to produce efficient nanowire-based solar cells with a solution-based process and using earth-abundant elements [36] can significantly reduce fabrication costs compared with existing high-temperature bulk material approaches.

2.4. *Copper indium diselenide (CIS) and related compounds*

Great improvements can be expected in the near future owing to the high flexibility of the design of compounds with defined properties in this material system (e.g., bandgap grading). A better understanding of the surface and junction properties of materials can lead to the development of various devices and result in new perspectives on ternary thin-film PV devices [33]. CIS is an effective material, but its complexity makes its manufacturing difficult. Safety can be considered as another concern in the manufacturing process [13]. Due to the composition, density, and adhesion properties of CIS, it can be useful in solar cells [37].

Table 2
Some summarized data for different types of Si solar cells.

Type	Advantages	Disadvantages	Limitations	Modifications
Single crystal Si	Abundant raw material supply, reasonably high efficiencies, low ecological impact, high stability, highly reliable outdoor applications	Complicated manufacturing method and high cost	Indirect bandgap type with lower absorption coefficients	Improving the Si etching [32–35], fabrication of quasi-single crystalline Si [36], antireflecting [37,38]
Polycrystalline Si	Low cost	Low conversion efficiency	Grain boundary and increased concentration of in-grain defects	Grain boundary passivation and metal finger net [39,40], texturing [34,41,42]
Amorphous Si	High light absorptivity, can be deposited on different inexpensive substrates, low total costs of materials and manufacturing	Low cell energy conversion efficiency, outdoor reliability problem	Staebler–Wronski effect (SWE), borderline structure between amorphous and crystalline Si	Decreasing the SWE [43], improving the material properties by hydrogen dilution of silane [44,45], improving the fabrication based on a Si:H technology on float glass [46], nanostructure tailoring of Si [47,48], using up-conversion materials [49]
Crystalline thin film Si	Can be deposited on inexpensive substrates, low total cost of materials	Low absorbance		Lambertian back side reflector or a textured front surface in combination with a reflecting back side [50], some transferring technologies of monocrystalline thin Si-films onto glass [51]
a-Si/c-Si heterostructures	Potential for high efficiency, very good surface passivation, low processing temperatures (below 200 °C), reduction of energy payback time			Heterojunction with intrinsic thin layer [52–55]

Table 3
The data and recommendations for future research directions.

Solar cell	Limiting material	Energy (TWy)	Recommendations
Poly/c-Si	Ag (n-electrode)	~2.5	Alternative electrodes
a-Si	In (TCO)	~0.1	Avoid ITO
	–	> 10	Improve efficiency
CdTe	Te (cell material)	0.02	NA-limited by cell material
CIGS	In (cell material)	0.02	NA-limited by cell material
Dye-sensitized	In (TCO)	~0.01	Alternative contacts
	Sn, Pt (TCO)	~5	Improve efficiency
Con. MJC III–V	Ge (substrate)	~0.02–0.2	Alt. substrate
	Ga (GaAs substrate)	~1–2	Lift-off, III–V/Si
Con. MJC III–V, lift-off	In (cell material)	~4	In-free multi-junction cells
	Au (electrode)	~	Alternative electrodes

Note: here one TWy is about 6 TWp.

2.5. Organic and other solar cells

2.5.1. Tandem cells and concentrating systems

Ultra-high efficiencies have been predicted for multijunction III–V solar cells if a satisfactory third junction material can be identified. GaInNAs alloy is a promising candidate because it can be grown on a lattice matched with GaAs with a 1 eV band gap [38].

Similar crystallinity or lattice structures in all layers between the top and bottom cells in a monolithic multijunction solar cell are necessary to obtain optical transparency and maximum current conductivity. A mismatch of crystal lattice constants induces deficiencies or dislocations in the lattice where centers of recombination can exist.

The lattice parameter currently limits the choice of III–V compounds; thus, metal organic chemical vapor deposition can monolithically develop the materials [39].

2.5.2. DSSCs

Improving the environmental stability of cells is the most important issue in studying these cells [40]. Other research issues include the identification and development of new dye molecules and suitable solid electrolytes for DSSCs with good efficiencies. Searching for new dyes (e.g., black dye) with better efficiencies can potentially improve the cell efficiency. Both dye and electrolyte must not undergo degradation. Finding infrared absorbing

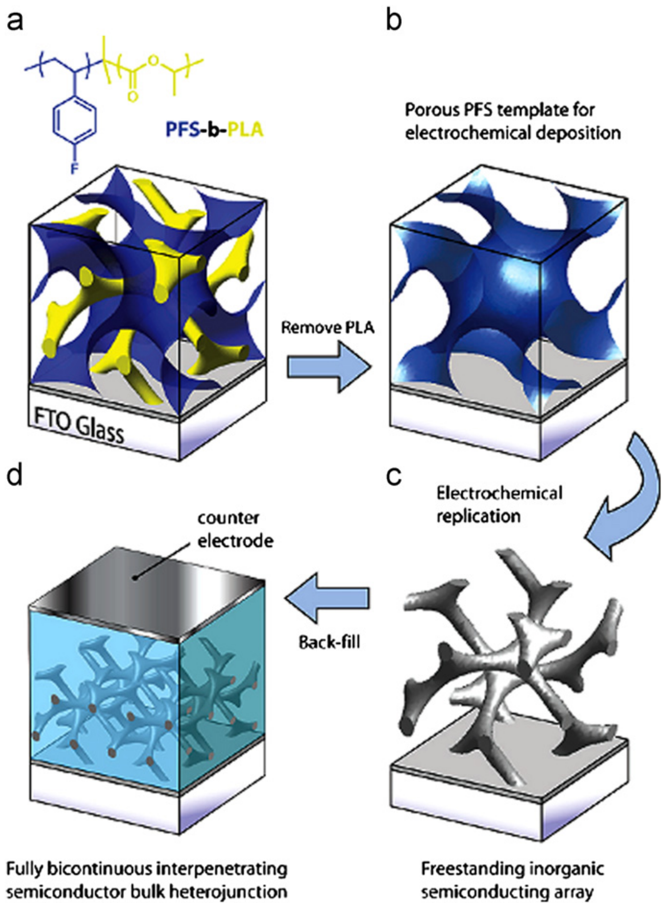


Fig. 6. Schematic representation of gyroid network replication from block copolymer templates and assembly of hybrid solar cells. (a) PFS-b-PLA gyroid block copolymer morphology (for clarity only the representative central gyroid surface is shown for the majority PFS block). The polymer is prepared as a film on a glass substrate with transparent conducting oxide coating (FTO glass). (b) Voided PFS gyroid template after selective removal of the minority PLA networks. Electrochemical replication of the voided network proceeds uniformly from the underlying substrate. (c) Freestanding gyroid network array after removal of the supporting PFS template. (d) Back-filling of the array with a solid state hole transporting material and capping with a suitable counter electrode produces a bicontinuous bulk heterojunction solar cell architecture.

dyes to produce transparent modules is another considerable long-term interest in this field [41].

The development of a new structure that can be utilized to "self-assemble" low-cost PV cells is another desirable goal. As shown in Fig. 6, the self-assembly of a solar cell starts with one of two polymers; one forms a "gyroid" shape and the other fills the surrounding space [42].

Recently, Kim et al. [43] reported a synthetic strategy of organic dyes to achieve high photovoltage for DSSCs. They employed organic dyes with non-planar spacer groups, and proved that non-planar geometry in organic dyes is one of the important factors that affect photovoltage.

Using natural dyes as sensitizers are promising since they are potential alternatives to expensive and rare organic dyes. They also offer environmental friendliness, low-cost production, designable polychrome modules, simple preparation technique, and wide availability. However, the disadvantage of using natural dyes is their low efficiencies for large-scale production, which warrants further research and development [44].

Recently, graphene sheets have been discovered able to act as electron bridges in DSSCs and increase their conductivity [45].

2.6. Organic, Hybrid, and composite materials for solar cells

A suitable polymer that has a conjugated chemical structure and good durability must be identified to develop solar cells. In this regard, excellent progress is being made on several fronts, with the main challenges being improved efficiency and durability [41]. These challenges in developing organic semiconductors for PV applications are considerable; hence, new materials, methods of manufacture, device architecture, substrates, and encapsulation materials are required.

Three different device structures are used with organic/plastic and hybrid cells [46], including single-layer device, double layer cell, and dispersed heterojuction cell. In the third device (known as a "bulk heterojunction"), the electron [47,48] and hole-accepting materials are mixed with the phase separation that occurs in the final stages of film preparation. Then, different materials with a diffuse interface must be prepared [41].

Three major issues are considered in conjugated polymer-based PV devices (bulk heterojunction solar cells), including (i) nano-morphology optimization [49], (ii) improvement of charge carrier mobility, and (iii) improvement of spectral sensitivity. Successful strategies toward improved PV performance are proposed using various novel materials, including double-cable polymers, regioregular polymers, and low-band-gap polymers [50,51]. Thin film adhesion onto polymer substrate is another challenging issue that can be addressed by choosing the proper substrate, etching, or bonding materials [52].

Sensitized nanomaterials and fullerene polymer composites also face significant difficulties. Both photodegradation and chemical degradation occur in these materials. These phenomena appear to be strongly dependent on the surface bonding and quality of the adsorption site for the molecules involved [53]. Further research is needed to optimize the surfaces of nanoparticles and increase the stability of the attachment of sensitizer molecules. At present, the preferred strategy to overcome these problems is to improve the sealing, which prevents access to oxygen and humidity. However, this strategy may counter the advantage of inexpensive production of materials. Therefore, a new strategy possibly based on the negative experience gained from dye sensitization and composite solar cells must be developed. Such new composite solar energy materials should not contain substances with inherent photodegredation properties, which currently exclude many organic materials and well-known semiconductors on a fine scale. After the identification of suitable stable materials, the key challenge is their chemical modification. The purpose is to make electron transfer from the absorber to the acceptor much more efficient than in the reverse reaction [15]. Some attempts have been made to develop complex structures using self-organization, which can be engineered from novel materials (e.g., discotic liquid crystals) by simple solution-processing steps and may realize inexpensive, high-performance, thin-film PV technology [54,55].

The molecular orbital mismatch between the donor polymer and acceptor molecules in organic photovoltaics (OPVs), which results in low voltage output, is one of the main causes of low device power conversion efficiencies (PCEs). Many researchers worked on OPVs using polymers as donors and a variety of C60 fullerenes with organic molecules attached as acceptors. Ross et al. [56] developed a novel fullerene species as acceptor materials for use in PV devices. This study provides a path toward achieving higher PCEs in OPV devices by demonstrating that high-yield charge separation can occur in OPV systems that have reduced donor/acceptor lowest unoccupied molecular orbital energy offset.

Another interesting area in this field includes the application of functionalized graphene as an active layer material for polymer solar cells [57].

3. Advanced high-efficiency solar cell concepts

This section is concerned with novel theoretical materials known as designer materials that would provide considerable benefits for photovoltaic conversion. They are principally designed to combine the effect of tandem cells in one material [33].

3.1. Auger generation material

In this concept, two or even more electron hole pairs should be generated by high-energy photons (energy greater than 2 EG) through impact ionization. Kolodinski [58] proposed the use of Ge superlattices. Si/Ge [59–62]or Si/SiO_2 superlattices can be alternatively utilized or certain QDs. These QDs can produce two or three excitons (electron–hole pairs) per photon that can tunnel or transfer (via polariton modes) from surface layers into the conduction band of 1 G or 2 G devices to enhance the effectiveness of solar cells. The finite flux of high-energy photons and the need for effects over a broad spectral range restrict the prospects for impact ionization. Similar to the aforementioned concepts, the simple addition of a cheap layer of self-organized structures that may enhance the device efficiency by 2% or 3% is the most practical solution [63]. The maximum impractical efficiency of such a material is 42% instead of 30% for a semiconductor with an optimal gap. The necessities for the band structure of such a material have been studied, but the synthesis of such material has not been undertaken yet. In accordance with [64], the new material should have an essential indirect gap of 0.95 eV and a direct gap of 1.9 eV. As a possible material, Si–Ge alloy has been introduced and studied [59,65] as a bottom cell material of triple-junction solar cells that enhances the sensitivity in the longer wavelength region because of its narrow energy gap [66,67]

3.2. Intermediate metallic band material

One longstanding problem in solar cell materials design is solved by the intermediate metallic band material. This material takes advantage of below-bandgap energy photons, thus enhancing the efficiency of solar cells above the Shockley and Queisser efficiency limit [68,69]. Photons with energies lower than the gap can be used if there is an intermediate energy level around the midgap through which two photons can transport the carriers from one band edge to the other. Unfortunately, such levels are also strong recombination centers and results in extreme quality degradation of the material. Placing a narrow metallic band within the gap of a wide gap semiconductor can at least theoretically overcome this problem. Non-radiative recombination is prevented by the intermediate band. Both holes and electrons exist as minority carriers, and charge neutrality is always created because of the metallic nature of the band.

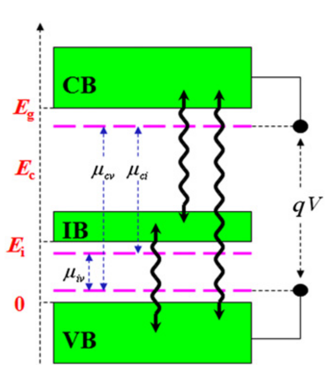


Fig. 7. Band diagram of a solar cell with an intermediate band [126].

Optimum absorption edges should be at 0.93, 1.40, and 2.43 eV. The theoretical efficiency of this device is 46.0%, compared with 41.9% of the previously described tandem cell. The intermediate band base material should be located between two ordinary semiconductors, one strongly n-doped and the other strongly p-doped (Fig. 7). Otherwise, the metallic band short circuits the device.

Marti et al. [70,71] proposed a technique for preparing intermediate band materials. The incorporation of QDs 35–70 Å in diameter of an appropriate ternary compound into another wider gap ternary material is proposed. The intermediate band solar cell concept can be practically accomplished using QDs, but its success depends on the resolution of a number of challenges. Further investigations have been performed using QD intermediate-band solar cells [72,73]. An intermediate band solar cell based on the ZnTeO material system has recently been evaluated both experimentally and theoretically [74]. The experimental result illustrated that ZnTeO-based cells have an expanded response to the solar spectrum compared with ZnTe owing to photo-excitation below the bandgap energy. Consequently, the short-circuit current approximately doubles and the open-circuit voltage decreases by about 15%.

Theoretical efficiency calculations of new types of solar cells have been extensively studied, and further research on materials and processing methods is necessary to achieve the desired efficiency. More investigations need to be conducted before solar cell performance can start approaching theoretical limits [71,75].

3.3. Bandgap engineering

A considerable amount of optical power is lost because of the large fraction of infrared light with insufficient energy to raise an electron into the conduction band (losses of sub-band gap). Only one electron can be raised to the conduction band by the high-energy photons, and the extra energy is wasted through heating the solar cell (hot-electron or thermalization losses). These basic losses directly result in an efficiency limit of about 40% and 43.9% for all commonly used semiconductors and single-junction Si solar cells, respectively [69]. Newly developed 3 G concepts have been formulated to salvage some of this wasted energy [11]. Some of the interesting 3 G concepts which were investigated during the last 30 years consisted of multi-junction systems such as tandem cells [76], the use of quantum wells and QDs to increase absorption [77], the use of fluorescent collectors [78,79], impact ionization to use the kinetic energy of carriers [58,80], utilization of impurity levels [81], and hot-electron influences [4,82].

Some suggested approaches for enhancing existing solar cells include changing the optical/material interactions by nano-texturing or plasmon absorption, using nanostructured material to modify the band gap of an existing material, or using nanostructures to modify the strain between two materials or the impact of dislocations [83].

Some of the 3 G concepts that deal with photon conversion processes include down-shifting, down-conversion (DC), and up-conversion (UC) that can convert the solar spectrum to a spectral distribution using surface layers and structures, providing better opportunities to the underlying device to absorb light. DC and UC are the most important among the three photon conversion processes. Given that both DC and UC are multi-photon processes, they can minimize thermalization and sub-band gap losses in a single junction photovoltaic [84]. These systems have been studied theoretically, and efficiencies of 63% for UC and 40% for DC are expected. Optimized up- and down-converters may be stacked behind and in front of an existing bi-facial solar cell, respectively, and may contribute to an increase in overall efficiency [85–87]. Recently, these processes [88,89] and potential

materials [90] for Si-PV applications have been reviewed. Richards [91] intensively studied the DC applications of rare-earth-doped phosphors for Si photovoltaic. The recent employment of UC material in solar cells shows promising results [92–96].

These types of conversion are efficiently performed by the routine use of non-linear optics (NLO) crystals. However, even the most effective NLO materials can only be operated at special wavelengths and angles of incidence, with almost high and often coherent optical densities. At present, NLO materials are apparently incapable of enhancing mainstream photovoltaics [4]. Further examples of rare-earth doping materials have been investigated, and a number of studies on novel materials with various chemical structures are currently conducted [84,90,91].

A number of practical systems for spectral conversion are based on QDs [97], rare-earth doping [98], and luminescent dyes [99]. In each case, an "optical" layer above a device is designed to absorb one set of photons and thereafter releases a set of more suitable photons [4]. These processes are associated with the generic difficulties related to the need for broad-band absorption across the wavelength ranges of interest (most of these systems possess very sharp spectral features) and the need for 100% efficiency (or transparency) in spectral regions near the band edge. The use of inhomogeneous broadening mechanisms can result in the broadband absorption. QDs can be easily accomplished by changing the size distribution of the dots. By contrast, for rare-earth doping systems, broadening needs variation in the material that supports the atoms, which is a challenging process. Mixtures of dyes are also required to extend absorption. In each case, extension of the absorption results in the broadening of the emission that usually decreases the efficiency of optical conversion. Accordingly, the spectral conversion will always be a difficult subject, and creation of very high-efficiency devices seems to be improbable [4]. Considering that the principal drivers in solar cell technology reduce cost and enhance efficiency, then the advances in nanotechnology can provide solutions to both problems either by improvement of current technologies or replacing them with alternative solutions [8,83,100]. The use of cheaper materials and designing low-cost manufacturing processes can reduce the cost of solar cells, and efficiency is dependent on the ability of the solar cell to save and transform the incident light. The contribution of nanotechnology on efficiency is mainly attributed to the ratio of large surface to volume area which can be achieved using nanoparticles.

Two nanotechnological methods for engineering solar cell materials prove to be promising. One of these methods employs thin films of metal oxide nanoparticles, such as titanium dioxide, doped with other elements, like nitrogen. Another strategy utilizes QDs or nanosized crystals that offer a high absorption of visible light. These semiconductors are very small, and they sensitize a metal oxide film by injecting electrons into the film to enhance the conversion of solar energy. In addition to doping, QD sensitization increases the visible light absorption of the metal oxide materials. Jin Zhang [100] reported that solar cell materials can be better fabricated by combining these two approaches rather than using each method individually.

Two promising avenues that may influence the commercial production can be anticipated for the exploitation of light. First, enhancing by 3–5% the effectiveness of the device with little extra cost is highly possible and may be easily done by QDs embedded in dielectric layers directly above traditional devices [97]. Second, spectral conversion can be used within fluorescent collectors [78,79], where large-area wave guiding layers comprising dye molecules, QDs, or nanocrystals can be utilized to centralize light into the sides of small-area p–n junctions. This process does not produce high-efficiency devices, but it reduces the semiconductor volume. To produce 20% efficient devices, two orders of magnitude less Si may be required [4,101]. The quantum size effect results from electrons and holes being squeezed into a dimension approaching a critical quantum parameter called the "exciton Bohr radius" [102]. Both the size and geometric dimensions of the confinement influence the quantization. Quantum wells, quantum wires, and QDs are one-, two-, and three-dimensional confinement geometries for charge carriers, respectively. The transformation from a wire shape to spherical dot can change the energy gap and the photosensitive properties of the material. Given that the surface of quantum-sized particles is extremely large compared with the volume, the changes in the surface of the particle play an important role and induces changes in some of its properties. The particle size can be controlled by experimental conditions that induce changes in the properties of the nanoparticles [103–105].

A major task in the fabrication and handling of quantum-sized particles is their stabilization in appropriate matrixes [106–108]. Considering that the coalescence of nanoparticles results in the loss in size-induced electronic properties, the precise control of the particle size, stability, and controllable reactivity of nanoparticles is necessary. Hence, nanoparticles should attach to the surface of a substrate or to other particles to prevent their coalescence [109]. The nanoparticles that are not properly stabilized can agglomerate to form bigger particles, losing their quantum properties. Hence, the chemical properties play a vital role for the fabrication and stabilization of QDs. The use of quantum-sized particles for band gap-tailored solar cells and photoelectrochemical materials had been reported [5,110,111]. Another significant advantage is that various materials with very low energy gaps may be applied in solar cells in the form of quantum-sized particles. Such materials that can be used as potential photosensitive solar energy materials that can agglomerate can be avoided, which presents a considerable challenge [41]. In addition to the possible use of QDs as spectral converters, Barnham and Duggan [77] also proposed the use of quantum wells and QDs to extend the band gap and provide multiple electrons from a single photon through impact ionization [58,82]. Quantum wells, quantum wires, or QDs can be utilized to engineer the band gap of materials. The growth of SiGe quantum wells or Ge QDs by chemical vapor deposition on a Si wafer serves as an example. SiGe offers regions of narrowed band gap providing enhanced absorption in the infrared. Such increases may continuously lead to enhanced absorption, but the quantum specifications also present carrier traps and more defective crystal growth, resulting in enhanced carrier recombination. To circumvent this phenomenon, QDs can be used in a layer that has been separated by a thin insulator. This condition should essentially decrease the loss mechanisms, but will also decrease carrier transfer from dot to bulk semiconductor.

The utilization of self-organized structures may be involved using a truly futuristic and nanotechnological approach to photovoltaics. To date, most of the mainstream PV has been based on layered and large-area devices. Using arrays of high densities of self-forming nanodevices would be an alternative. Various semiconductors in nanowire or nanorod forms have been grown by Kayes et al. [112] via vapor–liquid–solid techniques. Other seeded or selective growth techniques that offer small great-quality crystallites that can also create the nano-based devices are available. These approaches are advantageous because of the reduced material volume, similarity of device behavior, good crystalline growth on amorphous substrates, and prospects for multi-junctions that can result in higher efficiency [4].

Inhomogeneous broadening mechanisms results in broadband absorption. Changing the size distribution in the QDs would easily result in broad-band absorption [4]. The rainbow design is one of

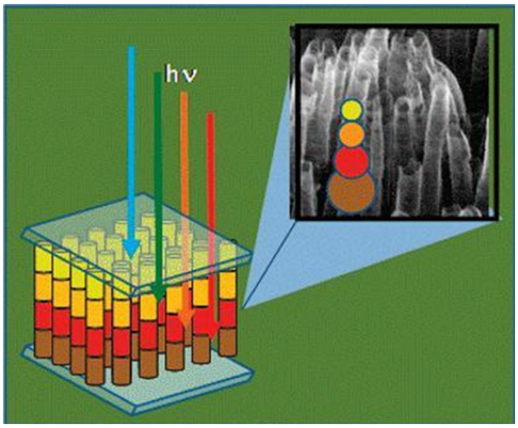


Fig. 8. Artistic impression of a rainbow solar cell assembled with different size CdSe quantum dots on TiO_2 nanotube array [127].

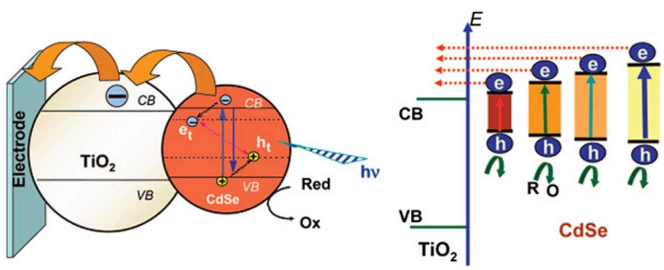


Fig. 9. Charge injection of excited CdSe quantum dot into TiO_2 nanoparticle. The scheme on the right shows the modulation of energy levels (and hence the charge injection) by size control [128].

the most interesting designs proposed by a team of researchers from the University of Notre Dame [103]. They claimed that the efficiency of a solar cell can be improved intensively by employing different sizes of QDs. Their rainbow design consisting of QDs arranged according to size enables each QD to absorb a specific wavelength of the electromagnetic spectrum resulting in optimum harvesting of the power light.

In the aforementioned study, the team created a single layer of QDs out of cadmium selenide on titanium dioxide tubes and nanofilms (Figs. 8 and 9). After absorbing light, the QDs emit an electron that conducts to the output electrode when electrons were injected into the titanium dioxide layer [103].

Researchers report the first efficient tandem solar cell based on colloidal QDs that may pave the way to inexpensive coatings that efficiently convert sunlight to electricity. They engineered a cascade or waterfall of nanometer-thick materials to shuttle electrons between the visible and infrared layers. This multi-junction solar cells made from a combination of PbS single QD materials with various sizes, and, bandgaps are therefore promising means to increase the energy harvested from the broad spectrum of sunlight [113].

Designed nanostructured surfaces probably offer routes which are optically more effective and may also be feasible to produce ultra-thin CdTe and CIGS-based thin-film devices. Here, the efficiency enhancements are of less importance than the decrease in the required thickness of the absorbing material and the proportionate decrease in cost. A final prospect for increased light collection has already resulted in plasmonics, which has appeared as a substantial technology [114–116]. Metal surface structures can back up the formation of resonant charge oscillations (plasmons) with finite lifetimes and diffusion lengths which can be accounted as a quasi-particle. Plasmonics can improve absorption as a consequence of the prolonged photon interaction at a device surface or may be utilized to increase scattering and direct photons into thin absorbing layers. Mulvaney [115] showed that by tuning the size of metallic nanostructures, the wavelength response can be modified to harvest a broad spectral range. This type of plasmonics application for solar cells using self-assembly methods to provide a cheap implementation route may be developed over the next 10–15 years [4]. Special attention should be given to QDs because they are predicted to be of utmost importance from the efficiency viewpoint. The arrangement of multiple layers of QDs, tuned to absorb various wavelengths, can theoretically achieve a total efficiency of approximately 86%. QDs can be placed on rigid matrices and electrically performing polymer supports to offer flexible solar cells.

The only proved 3G technology is based on using multiple junctions [41,117,118]. At the device level, crucial requirements include material growth, bonding and insulation. The use of nanotechnology, principles of self-alignment, and self-organization may effectively assist the solution of some of these problems over the next 20 years. The most favorable prospect for multi-junction approaches in the future may be based on polymer semiconductors or combinations of polymer semiconductors with crystalline semiconductors. Self-organized semiconducting polymer structures in multi-junction arrangements are predicted to be the mainstream of 50% efficient photovoltaic technology by 2050 [4]. Enhancing the use of new and 3 G technologies is expected to increase the performance (or decrease the cost) of 1 G and 2 G solar cells. These technologies most probably comprise some multi-junction concepts and are created based on the emerging fields of optical metamaterials, plasmonics, quantum technology, nanotechnology, and polymer semiconductor science [4].

4. Cost and economic

Wafering causes approximately half of the manufacturing cost for single Si modules, which is a time-consuming and costly batch process, in which thin wafers with thicknesses not less than 200 μm are cut from ingots. The whole wafer will break in wafering and subsequent processing if the wafers are too thin. A PV cell needs a large amount of raw Si because of this thickness requirement, and half of this high-cost material is lost as sawdust in wafering [13].

Polycrystalline Si is stronger than single-crystalline Si and can be cut into one-third the thickness of single-crystal material. This material is advantageous because of its slightly lower wafer cost and less strict growth requirements. However, their lower manufacturing cost is balanced by a lower cell efficiency [13].

The current technology is relatively mature, but several previous studies have revealed its potential for large cost reduction. Similar to other industrial products, the cost of manufacturing follows a learning curve that shows a cost drop of 20% for every doubling of manufacturing volume [33].

Aggressive development of non-Si-based PV materials has changed the PV landscape, offering exciting near-term cost reductions for material systems such as CIGS and CdTe. Quantifying material cost and the availability of these and other emerging material systems provides a critical measure to guide future research and development decisions toward a greatly expanded solar cell industry. To evaluate a new set of technical and economic performance targets, Wadia et al. [119] examined material extraction costs and supply constraints for 23 promising semiconducting materials. The maximum TWh and minimum ¢/W of each of materials were calculated to evaluate the electricity contribution and cost impact of material extraction to a finished solar module (Figs. 10 and 11). They find that devices performing below 10% PCEs deliver the same life time energy output as those above 20% when a 3/4 material reduction is achieved [119].

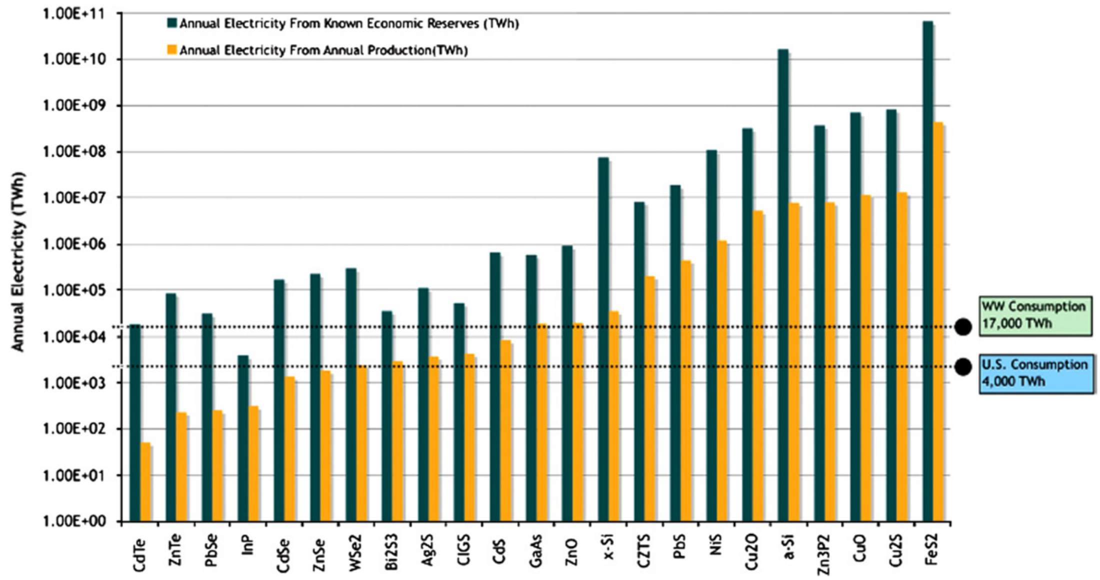


Fig. 10. Annual electricity production potential for 23 inorganic photovoltaic materials. Known economic reserves (also known as reserve base) and annual production are taken from the U.S. Geological Survey studies [129]. Total U.S. and worldwide annual electricity consumption are labeled on the figure for comparison [119].

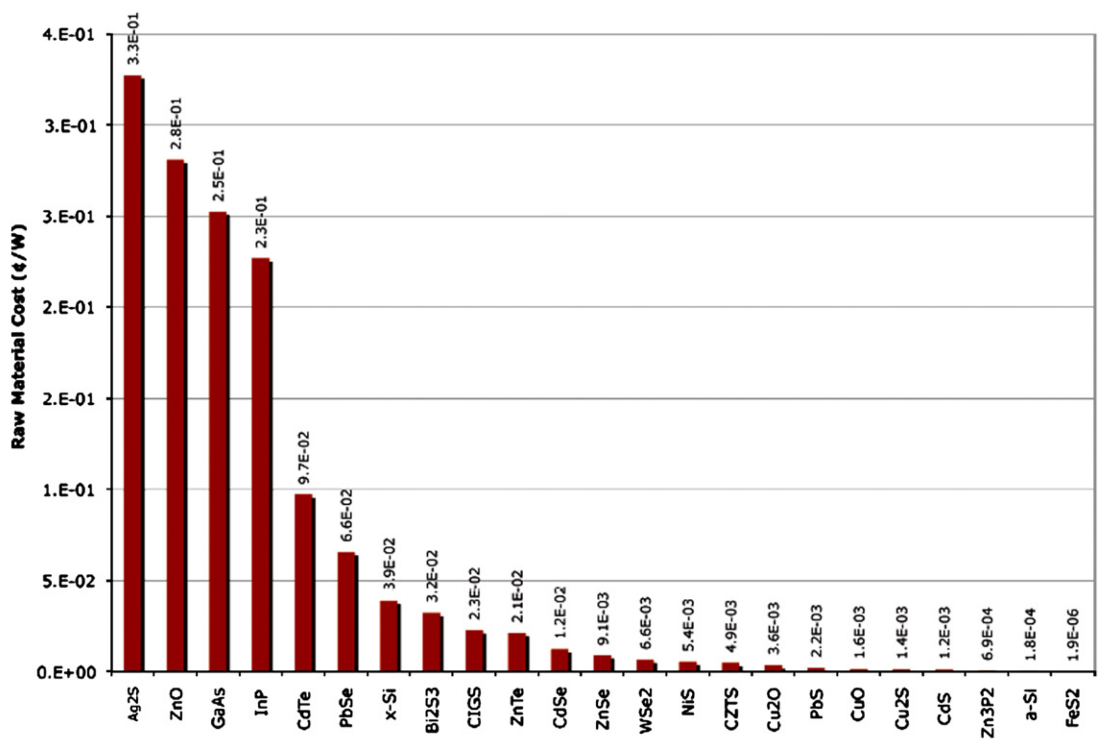


Fig. 11. Minimum ¢/W for 23 inorganic photovoltaic materials. Component cost contribution in ¢/W is a strong indicator of value for future deployment. Calculated values for all 23 compounds evaluated are shown. The range of costs are between 0.327 ¢/W for Ag_2S and < 0.00000 2 ¢/W for FeS_2. While the actual dollar figure per watt for material extraction will appear small compared to the entire cost of an installed PV system, the cost of processing the material for PV grade applications is a larger cost contributor and should be evaluated further [119].

4.1. Materials consideration

A number of researchers have investigated material availability issues for large scale PV production since the late 1990s [119–124].

Feltrin and Freundlich [125] investigated and summarized current material challenges for many existing technologies that play an important role in the present sub-gigawatt energy production levels preventing their scale-up to the terawatt range. Results obtained in this study that show limiting materials and identify improvements, as well as innovations, needed for further scale-up are summarized in Table 3. Although this study emphasized that the estimations are based on very simplistic and possibly optimistic assumption and thus should only be used

qualitatively, this study provided a new perspective for further studies.

5. Conclusion

Despite the introduction of new materials such as QDs, new dyes, and multilayer of ultrathin nanocrystalline materials, among others, the availability of sufficient quantities of raw material, inexpensive purification or synthesis, as well as deposition methods, and easy process control to achieve a large-area product within acceptable performance tolerances with high life expectancy are still the main challenges for solar cells. Therefore, to achieve the main objectives of photovoltaics, the efficiency of solar cells should be improved without any compromise on the processing cost of these devices. In short, materials chemistry plays a critical role in achieving the goals. Therefore, the device fundamentals based on materials chemistry should be incorporated effectively.

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